

REPORT DOCUMENTATION PAGE					Form Approved OMB No. 0704-0188	
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1. REPORT DATE (DD-MM-YYYY) 02-11-2009		2. REPORT TYPE Final		3. DATES COVERED (From - To) February 7, 2005 – January 31, 2009		
4. TITLE AND SUBTITLE DURABILITY OF COMPOSITE MATERIALS AND STRUCTURES				5a. CONTRACT NUMBER		
				5b. GRANT NUMBER N00014-05-1-0341		
				5c. PROGRAM ELEMENT NUMBER		
				5d. PROJECT NUMBER		
6. AUTHOR(S) Richard Granata, William Hartt, Leif Carlsson, Hassan Mahfuz, Lawrence Drzal, Dayakar Penumadu, Clive Clayton, William Scott				5e. TASK NUMBER		
				5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Division of Research, ADM-236 Florida Atlantic University 777 Glades Road Boca Raton, FL 33431-0991				8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Code 0332 Office of Naval Research 875 N. Randolph Street Arlington, VA 22203-1995				10. SPONSOR/MONITOR'S ACRONYM(S)		
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION/AVAILABILITY STATEMENT Unlimited						
13. SUPPLEMENTARY NOTES						
14. ABSTRACT This project focused on marine composites and sandwich structures with specific interests on the effects of moisture, seawater, hydrostatic pressure, and temperature on their durability and life prediction. One task revealed fiber changes that occur with nitric acid treatment promoting better engineering design of composite fiber/matrix interface and interphase region. Comparative environmental exposures show that moisture absorption was along the F/M interface (wickling). A fracture mechanical model of single fiber tests characterized the fiber/matrix interface toughness as a parameter to monitor degradation and fiber/matrix interface quality. For sandwich foam composites with nanophased core, improvement in debond fracture toughness (G _c) was significant (values increased 80 - 290% with SiC nanoparticle loading of 0.1-0.3 wt%). Composite flexural properties degraded with seawater immersion showing more significant strength loss for electrochemically polarized specimens. Using UV-ozone treatments, three sizing/surface treatments (epoxy, thiol modified coupling agent and maleic anhydride) have been found to increase the fiber-matrix adhesion ~50% between AS4 fiber and vinyl ester. For -40°C to 70°C, the effect of hydrostatic pressure to understand coupled behavior of temperature, seawater, and water head on mechanical behavior of polymeric composites and sandwich structures was evaluated. Toray FOE sizing from carbon fibers was isolated for characterization.						
15. SUBJECT TERMS marine composites, vinyl ester, carbon fiber, moisture, seawater, hydrostatic pressure, temperature, interface, durability						
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 14	19a. NAME OF RESPONSIBLE PERSON Richard Granata	
a. REPORT U	b. ABSTRACT U	c. THIS PAGE U			19b. TELEPHONE NUMBER (Include area code) 954-924-7237	

FINAL TECHNICAL REPORT

Prepared for

Office of Naval Research
Solid Mechanics Program Code 322

Program Manager: Dr. Yapa D.S. Rajapakse
Office of Naval Research
875 N. Randolph Street
Arlington, VA 22203-1995

DURABILITY OF COMPOSITE MATERIALS AND STRUCTURES

Period of Performance: February 7, 2005 – January 31, 2009

Award Number: **N00014-05-1-0341**

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November 2, 2009

20091110069

DURABILITY OF COMPOSITE MATERIALS AND STRUCTURES

Award Number: N00014-05-1-0341

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OBJECTIVES

Polymer-based composite materials have an important and growing role in naval vehicles and structures. Research on durability of composite materials subjected to environmental stresses is vitally important to reliable, efficient and affordable naval structures. The optimization of composite materials structures' mechanical-structural properties is developing steadily. However, environmental interactions and deterioration processes diminish actual performance of as-built structures and can have strong influences on designs of new structures.

This project was focused on marine composites and sandwich structures with specific interests on the effects of moisture, seawater, hydrostatic pressure, and temperature on their durability and life prediction. The main goals of this project were:

- i) To provide a better understanding regarding performance and deterioration mechanisms of composite materials in marine environments.
- ii) To enable enhancement of readiness and to produce cost savings by determination of environmental interactions and deterioration processes that diminish actual performance.
- iii) To develop guidelines for design and performance that enhance environmental and in-service durability.

TECHNICAL APPROACH

Moisture and salt are the primary aggressive agents causing deterioration of composite materials in the marine environment. The agents can directly degrade the components of the composite material by leaching the dispersed phase, modifying the properties of the matrix phase and disrupting the interface between phases. Saturation of the material surface with marine salts can enhance the moisture sorption of the material due to hygroscopicity of the salt-laden surface. High moisture environments (greater than 50%

relative humidity) can have profound effects on the polymer/dispersed phase properties. Uptake of water can decrease the glass transition temperature of the polymer changing the strength or toughness of the composite. Sorbed water can degrade the adhesive strength of the polymer-dispersed phase. Infused water can segregate into an aqueous phase within the polymer, particularly in the presence of ionic impurities or infused sea salt. In addition to these physicochemical processes, chemical hydrolysis of the polymer, the surface treatment or the dispersed phase leads to degradation of the composite whose properties are dependent upon the stability of the system. Also, cathodic protection that is used on ocean vessels and structures can have strongly degrading effects on conductive composites or non-conductive composites attached to conductive components. Substantial work (elsewhere) has been accomplished based upon mechanical studies involving environmental exposure of specimens. However, significant difficulties have been noted regarding the development of adequate understanding leading to prevention or solution of degradation problems.

To address the goals of this project a collaborative multidisciplinary approach was taken by integration of nine topics, described in the next paragraph. The mechanisms involved in polymer composites degradation was directed toward the fiber/matrix interfacial level. Mechanical, physical, chemical and electrochemical parameters were included to aid resolution of the complex interactions that result in deterioration. Mechanical testing methods were developed and applied to acquire a better understanding of the composite material interface durability. Surface characterization and modification of carbon fiber was also investigated.

The following topics describe in detail the studies performed in this project:

- Topic 1 – Durability of modified composite material interfaces.
- Topic 2 – Effects of hygrothermal history on the water sorption of carbon fiber/vinylester composites.
- Topic 3 – Evaluation of water degradation of polymer matrix composites by micromechanical and macromechanical tests.
- Topic 4 – Durability of sandwich composites with nanophased cores under sea environments.
- Topic 5 – Influence of cathodic protection on interfacial degradation in composite materials.
- Topic 6 – Engineering the fiber-matrix interphase for naval structural composite systems.
- Topic 7 – Evaluation of the effects of sea water and freezing temperature on the deformation and integrity of polymeric naval composite materials and sandwich structure using advanced experiments and analytical models.
- Topic 8 – Surface and Interfacial Analysis for the Determination of Polymer-fiber Degradation.
- Topic 9 – Laser Pumped Fluorescence for Nondestructive Assessment of Durability for Composite Materials and Structures.

PROGRESS

This section summarizes the accomplishments of each research topic addressed within the contract in the period of February 7, 2005 – January 31, 2009.

1. Durability of modified composite material interfaces (Topic 1)

Dr. Richard D. Granata, PI
Florida Atlantic University
Department of Ocean and Mechanical Engineering

1.1 Objective

The objectives of this research segment include: a) modification of carbon fiber surfaces with nitric acid oxidation; b) determining fiber physical properties of surface morphology, diameter and tensile strength; c) measuring the surface energies and types of surface oxidation as hydroxyl, carbonyl and carboxyl moieties; and d) evaluating basic properties of composite materials prepared with modified fibers.

1.2 Approach

Carbon fibers were treated with boiling nitric acid. Their surface morphology and diameter were evaluated using scanning electron microscopy while mechanical tests determined tensile strength. Surface properties were determined using derivative x-ray photoelectron spectroscopy, scanning electron microscopy and surface tensiometry. Subsequently, transverse tensile tests were performed on composites fabricated from treated fibers and vinylester resin.

1.3 Accomplishments

High strength (Type II) PAN-based carbon fibers were treated with varying lengths of nitric acid exposure. Fiber physical properties were evaluated, including surface morphology, diameter, and tensile strength. Surface properties were also investigated by determining the distribution of hydroxyl, carbonyl and carboxyl groups, as well as the levels of polar, dispersive and total surface energy. No evidence of pitting or uneven surface degradation was found, but fiber diameter decreased with time. When considering diameter changes, fiber tensile strength improved to a constant level, suggesting that the strength gains were due to the mitigation of surface flaws. Carbonyl and carboxylic acid group concentrations both increased significantly with nitric acid treatment time, whereas hydroxyl groups did not. Total free surface energy also markedly increased, due to the polar component, while the dispersive energy component declined. The increased concentrations of carbonyl and carboxylic acid groups are expected to improve composite fiber/matrix chemical bonding and the increased surface energy is expected to impact composite fiber/matrix wetting.

Overall, this work (Topic 1) provides a view of the many fiber changes that occur with nitric acid treatment. It is imperative to better understand these effects so that changes in resulting composites can be predicted and understood. This current treatment, with these fiber types, leads to reduced-diameter fibers with smooth surfaces and improved tensile strength, allowing for more of the smaller, higher-strength fibers to be packed into the composite. Their smooth surfaces limit the possibility of mechanical bonding between themselves and the matrix. Higher surface energy suggests better fiber wettability, which

may lead to reduced composite void content, provided that fiber cohesion doesn't create problems in this sense. And finally, increased concentrations of reactive chemical groups on the surface provide an opportunity for chemical bonding between the fiber and matrix, and a better understanding of the surface group types allows for better engineering design of the composite fiber/matrix interface and interphase region.

2. Effects of hygrothermal history on the water sorption of carbon fiber/vinylester composites (Topic 2)

Dr. Richard D. Granata, PI
Florida Atlantic University
Department of Ocean and Mechanical Engineering

2.1 Objective

Although extensive studies have been performed on real life conditions or in particular environments, analyses of effects due to the exposure history of water absorption in resins and composites rarely appear in scientific literature. The reversibility of wet/dry cycle, the damage induced by the absorption process, the effect of this damage on the later stages of the absorption process and on subsequent cycles, is of practical interest.

The aim of topic 2 was to study the effect of cyclic absorption process on the mechanical properties of carbon fibers/vinylester composites.

2.2 Approach

The cyclic water absorption behavior of vinylester (VE) matrix and their composites with unidirectional carbon fiber (CF) was studied. The specimens were immersed in distilled water (DW) at room temperature (RT), and seawater (SW) at RT, 40, and 60°C, respectively. The water uptake tests were carried out in two immersion cycles to investigate the effect of previous history on sorption behavior and the reversibility of the wet/dry cycle. The first cycle was completed when the specimens reached the water saturation content. After that, the specimens were dried until constant weight was observed. Then dry specimens were then returned to their environmental immersion bath. The weight change was determined again. The viscoelastic properties were measured on dry and moisture saturated specimens after first and second immersion cycle. Transverse tensile tests and microstructural analysis were also performed on composite specimens under the same exposure conditions.

2.3 Accomplishments

Moisture absorption of neat VE resin and CF/VE composites at the different exposure conditions was investigated. The moisture content of the neat resin specimens increases with time, temperature, and exposure cycle. Higher slopes of the initially linear section of the curve were observed at higher exposure temperatures indicating a higher rate of moisture transport. However, the moisture content of specimens immersed in seawater at 60°C decreased after having reached maximum moisture content, specially after the second immersion cycle, possibly as a result of leaching constituents from the resin and chain breakage resulting in smaller molecules. As general results, in the first cycle the water absorbed was lower than in the second cycle.

The composite specimens absorbed more moisture than the neat resin specimens. Taking into account that the composites contain only about 36% resin and that carbon fibers do not absorb water, it becomes evident that the moisture absorption was along the F/M interface (wicking) because no cracks or voids in the material were observed before immersion. This indicates that for composites water absorption is an interface-dominated phenomenon. The main differences were observed in the second immersion cycle. Specimens subjected at SW 60°C demonstrated a continuous weight-gain and saturation was not reached for both cycles.

Water exposure did not affect the viscoelastic properties of the neat resin. No change in the glass transition temperature, T_g , was observed.

However, for the composite specimens, the T_g decreased 9°C after water exposure. A possible explanation for that change involves a specific evolution of the macromolecular network at the fiber/matrix interface during the hygrothermal conditioning. Although it is not possible to identify these processes from a chemical point of view, it is possible to conclude that these processes affect the interface sufficiently to modify the relaxation mechanisms associated with the α -transition. The movement of the polymeric chain is more difficult for higher interface adhesion. Therefore, the interface adhesion increases the T_g . Because the water exposure reduces the T_g , it is expected that the interface adhesion is also reduced. Furthermore, the T_g was completely recovered after drying the specimens indicating that the reduction was a reversible process.

The storage modulus, E' , was also reduced for all specimens after water immersion. Moreover E' slightly decreases when the exposure temperature increases. But this change in the modulus is permanent because no recovery was observed after drying the specimens.

The results also show that for storage modulus and T_g no relevant differences were observed between the two immersion cycles at the studied hygrothermal conditions.

The transverse tensile properties decrease with water immersion but the strength drop is higher than the modulus loss. After the second immersion cycle the same tendency was observed but the reduction in the tensile strength values were more prominent. This reduction of the transverse strength was attributed to the degradation of the F/M interface strength, because no degradation of the matrix was found.

3. Evaluation of water degradation of polymer matrix composites by micromechanical and macromechanical Tests (Topic 3)

Dr. Leif A. Carlsson, Co-PI
Florida Atlantic University
Department of Ocean and Mechanical Engineering

3.1 Objective

The main objective of this section of the project is to experimentally investigate the durability of the constituents of marine composites used in naval applications, i.e. carbon and glass fibers, vinylester and epoxy matrix materials, and the fiber/matrix interface, immersed in distilled water and seawater.

3.2 Approach

The degradation of carbon/vinylester, carbon/epoxy, E-glass/vinylester, and E-glass/epoxy composites subjected to water (distilled water at room temperature (RT) and seawater at RT, 40, and 60°C) was investigated. Water absorption behavior of the neat resins and composite specimens was examined. The tensile strength of the dry and water immersed fibers was monitored using the single filament test (SFT). The mechanical properties of dry and water immersed matrix materials were monitored by tensile, compressive, flexure, and dynamic-mechanical tests. The integrity and durability of the fiber/matrix interface of the composite systems were studied using the single fiber fragmentation (SFFT) and Outwater-Murphy (OM) tests. The Broutman test was also explored. Results were correlated to transverse tensile and transverse flexure strengths of composites. In addition, fracture mechanics models were developed for determining the fracture toughness of the fiber/matrix interface based on testes of the SFFT and OM specimen. Design analyses of the OM and Broutman test were conducted.

3.3 Accomplishment

Neat epoxy absorbed much more water than neat vinylester. The vinylester matrix composites absorbed more moisture than the neat resins, which was not expected because the resin volume fraction is only about 36% and the carbon fibers do not absorb water. The epoxy matrix composites, on the other hand, absorbed less moisture than the neat epoxy resin, but more than expected based on the 36% resin volume fraction. The difference in moisture absorption behavior between composites and neat resins are attributed to wicking as a water absorbing mechanism.

The flexure test performed on the neat resins show that the vinylester matrices were not significantly affected by exposure to water while the strength of the epoxy was reduced by a factor of 2.

Single fiber fragmentation test revealed large extents of fiber/matrix debonding and substantial reductions in the fiber/matrix interface shear strength of all systems after exposure to water. OM testing of dry C/VE and G/VE specimens revealed that glass and carbon fiber displayed similar adhesion to vinylester in the dry state. Absorption of water severely degraded the fiber/matrix adhesion for the carbon fiber with general purpose sizing and the glass fiber. A notable exception was carbon fiber with FOE sizing. This sizing produced a strong and durable interface that was not debonded in most of the environmental conditions examined.

Transverse tensile and flexure tests were performed on composite specimens to monitor the influence of fiber/matrix interface on macroscopic behavior. Large reductions in transverse strength of the water immersed composites were experienced for all systems as a result of matrix and fiber/matrix interface degradation by water.

A fracture mechanical model of the single fiber tests was developed to characterize the fiber/matrix interface toughness, as a parameter to monitor the degradation and quality of the fiber/matrix interface.

4. Durability of sandwich composites with nanophased cores under sea environments (Topic 4)

Dr. Hassan Mahfuz, Co-PI
Florida Atlantic University
Department of Ocean and Mechanical Engineering

4.1 Objective

The main objectives of the study were to develop a nanophased core material for sandwich structures which would improve upon the mechanical and fracture properties of the core as well as that of the sandwich composites and evaluate environmental effects such as temperature and moisture in the fracture toughness properties.

4.2 Approach

Polymer foam system widely used in marine industries was identified and was reinforced with low loading of SiC nanoparticles.

Mechanical and fracture properties were determined to verify any improvement.

4.3 Accomplishment

Reinforcement of SiC nanoparticles significantly improved the compressive and flexural properties ranging from 50-200% over the polyurethane foam. The tensile modulus was slightly reduced but fracture strain improved by about 70%.

Fracture properties of the foam in the flow direction were somewhat reduced by SiC reinforcement. When nanoparticles were functionalized, fracture properties recovered to the level of neat foam. On the other hand, fracture data in the rise direction were close to that of the neat foam even without functionalization.

For sandwich composites with nanophased core, the improvement in debond fracture toughness (G_c) was significant. The values increased by 80 - 290% with various concentrations of nanoparticles. Highest enhancement was observed with lower loading of nanoparticles; 0.1-0.3 wt%.

5. Influence of cathodic protection on interfacial degradation in composite materials (Topic 5)

Dr. William Hartt, Co-PI
Florida Atlantic University
Department of Ocean and Mechanical Engineering

5.1 Objectives

The objective of this study is to determine the influence of cathodic protection on interfacial degradation on composite materials and identify the deterioration processes that occur for the composite.

5.2 Approach

Vinylester resin (VE, Derakane Momentum 411-350, Ashland Chemical Co.) containing 45 wt% styrene was used as the composite matrix. Carbon fibers (T700, F sizing, Toray) in unidirectional architecture were used as reinforcement. Carbon fiber/vinylester composites were fabricated using vacuum assisted resin transfer molding (VARTM) process at RT. The plates were post-cured at 124°C for 2 h. After cathodic polarization, two types of tests were carried out: electrochemical impedance spectroscopy (EIS) test and four-point bending mechanical test. Electrical connections to the CF were made using nickel print coating (GC Electronics # 22-207) to connect copper wire and one side of the composite with exposed fiber ends. After 24 h epoxy resin was used to seal the electrical connection by top-coating the nickel coating. Epoxy resin was also used to seal the other three sides of specimens and was allowed to cure for 24 h prior to the initiation of immersion. After the samples were polarized cathodically in seawater for 1-9 months, properties tests were carried out, including EIS and four-point bending tests.

5.3 Accomplishments

Experimental methods were developed for evaluating the electrochemical properties of conductive CF/VE composites.

CF/VE composites electrochemical properties have similarities to noble metals (Au or Pt).

Specimens for combined electrochemical and mechanical properties testing were fabricated and immersed in seawater.

Upon visual inspection of the CF/VE composites that have been subject to constant potentials, it was found that different amounts of calcareous deposits had formed at the surface of the composite. The build up of these deposits was usually greater at one face. It was decided to investigate further by observing samples under the light microscope and also ESEM, in the case where the build up was significant it was possible to subject a piece of the sample to x-ray diffraction analysis to identify compounds present. It is important to mention that evidence of blisters was not observed in contrast to polarized CF composites studies from Brown (Long Island Group).

Composite flexural properties were degraded after seawater immersion, strength loss was more significant for the higher potential used.

6. Engineering the fiber-matrix interphase for naval structural composite systems (Topic 6)

Dr. Lawrence Drzal, Subcontractor
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6.1 Objectives

The objectives of this work are: a) to develop a model 'engineered interphase' for a carbon fiber-vinylester matrix system having interfacial properties comparable to an

aerospace carbon fiber-epoxy system, and, b) to develop a practical 'engineered interphase' for a carbon fiber-ambient cure, epoxy matrix system having interfacial properties comparable to an aerospace carbon fiber-epoxy system.

6.2 Approach

The following approach was taken: a) identify the physical and chemical interactions between carbon fibers combined with vinylester and epoxy matrices in composite materials; b) modify the surface chemistry and interphase structure in the carbon fiber-vinylester and carbon fiber-epoxy systems to improve fiber-matrix adhesion levels to that of CF/epoxy; and c) quantify the in-situ CF-VE matrix adhesion and interphase mechanical properties as well as composite laminate properties.

6.3 Accomplishment

Research continued on the surface characterization of AS4 treated with UV-ozone treatment of AS4 carbon fibers at 60 seconds of exposure that increased the surface oxygen percentage from 13% to 18% with a slight increase of the roughness, and reduction in tensile strength.

The interfacial shear strength of the AS4 fiber treated with UV/Ozone increased about 40%, from 26 ± 4 MPa to 36 ± 3 MPa in epoxy.

The microindentation test has been successfully applied to measure adhesion of carbon fibers to Derakane 510A-40 vinylester resin matrices.

Optimal conditions (drying temperature, speed of winding, concentration of the sizing solution) were identified for continuous coating (sizing) of carbon fibers with the use of a Sizing Tower System.

Three sizing/surface treatments (i) Epoxy sizing; ii) thiol modified coupling agent (11-Mercaptoundecanoic acid); and iii) maleic anhydride) have been found to increase the fiber-matrix adhesion ~50% between the AS4 fiber and the vinylester matrix.

7. Evaluation of the effects of sea water and freezing temperature on the deformation and integrity of polymeric naval composite materials and sandwich structure using advanced experiments and analytical models (Topic 7)

Dr. Dayakar Penumadu, Subcontractor
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7.1 Objectives

The objectives of this work were to evaluate the effects of sea water and freezing temperature on the deformation and the integrity of polymeric naval composite materials and sandwich structure using advanced experiments and analytical models.

7.2 Approach

The approach taken was complete a set of tasks in support of the objectives including:
a) Complete the collection of expansion data for both facings and foam core material.

Generalize the theoretical shear-lag model to the case of non-parallel facings. b) Immerse closed cell foam samples in sea water, including cases under hydrostatic pressure, and explore the subsequent effects of freeze and thaw. c) Investigate the effect of pre-immersion in seawater on the aging of T700 carbon fibers/vinylester composite utilized as facings in sandwich structures. d) Immerse H100 closed cell foams under various levels of hydrostatic pressure and correlated permeability and flow to pressure. d) To study the effects of freeze/thaw on delamination toughness of sandwich layers.

7.3 Accomplishments

Fabricated chambers and integrated large environmental chamber with servo-hydraulic testing systems for mechanical testing of foam and facing materials, and for fracture toughness measurements of sandwich composites, for a temperature range of -40°C to 70°C anticipated for naval structures were developed.

Advanced analytical and numerical models were developed including shear lag modeling for curved sandwich lay-ups using displacement-based approach to model the effect of seawater or temperature induced strains on the integrity of sandwich structures.

A fundamental understanding of the effects of freezing and freeze/thaw on material properties (G, E) of PVC foam core including fracture toughness and interfacial delamination toughness was developed.

The effect of hydrostatic pressure to understand the coupled behavior of temperature, seawater, and water head on the mechanical behavior of polymeric composites and sandwich structures was evaluated.

8. Surface and Interfacial Analysis for the Determination of Polymer-fiber Degradation (Topic 8)

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8.1 Objectives

The first objective of this project is to characterize the chemical composition of the existing fiber sizing, to relate this characterization to apparent degradation at the interphase, and to assist group members in designing the "engineered interphase". The second objective of this project is to relate environmental damage and weathering to chemical changes in the composite sample, and to relate this information to the change in mechanical properties.

8.2 Approach

Spectroscopic methods were used to characterize the chemistry of the provided composite samples. Raman, FTIR and XPS techniques were applied to virgin and damaged composites, to investigate chemical changes. From this characterization, degradation pathways and chemical influences were determined. Samples were exposed to UV radiation and to heat, both in the presence and absence of moisture to determine

the effect of bound water. Spectroscopic methods were further used to analyze the existing sizing on the provided Toray T700 carbon fibers. The sizing was extracted, and subjected to the same environmental conditions and analyzed for degradation. The chemistry of this sizing at the interphase to the matrix was investigated through the creation of a free-standing interphase.

8.3 Accomplishments

Toray FOE sizing from carbon fibers was isolated for characterization and environmental exposure.

Layers of resins were removed from the CF/VE composite by ultra fast (athermal) laser ablation in order to facilitate the direct exposure of the fiber/matrix interface to the environment. However, severe composite fracture as a result of heterogeneity through laser ablation was observed.

Thermally-damage of the CF/VE composites was examined by shifts in fluorescence.

CF/VE specimens were exposed to UV radiation.

9. Laser Pumped Fluorescence for Nondestructive Assessment of Durability for Composite Materials and Structures (Topic 9)

Dr. William R. Scott, Subcontractor
Computer Interface Instrumentation, Inc.
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Furlong, PA 18925

9.1 Objectives

The objective of this effort was to detect and characterize the effects of environmental attack on composite matrices using LPF (laser pumped fluorescence) spectroscopy. In addition, the use of thermography as a possible tool for investigation of mechanical and other types of degradation was explored.

9.2 Approach

Previous studies of carbon fiber/epoxy composites have shown that exposure to temperatures in the vicinity of T_g resulted in property degradation that is enhanced by moisture exposure. This type of damage is not detectable using conventional nondestructive testing methods such as ultrasonics or radiography, because it affects the chemistry of the resin rather than producing a physical discontinuity. On the other hand, methods such as laser pumped fluorescence (LPF) and Raman spectroscopy are able to interrogate materials on the molecular level and are sensitive to chemical changes associated with the thermal history of a material. The former method is of special interest for Navy applications because instruments may soon become available for applying it to real structures. In addition, chemical effects, changes such as micro-cracking and fiber breakage are also difficult to detect with conventional inspection tools. The use of acoustic emission monitoring may be effective in determining whether such degradation is taking place along with the chemical processes.

9.3 Accomplishment

A relationship between thermal exposure and LPF measurements for unidirectional carbon fiber/vinylester composites was established. Interaction between saltwater absorption and thermal exposure was observed.

Results of LPF measurements using different Raman spectra measurements were correlated.

NAVY RELEVANCE

This project has addressed a fundamental question of national security concerning the integrity of the Navy's defense systems. Specifically, from what materials will the next generation of naval vessels be constructed?

The improved understanding of environmentally induced deterioration mechanisms of composite materials developed in this project could help screen fibers and matrix materials and fiber sizings to achieve durable composites for naval applications. The mechanisms and macroscopic test results are valuable for designers of composite naval vessels.

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